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AEOSR-TR- 93 0497

A Final Report for:
ION DOPED QUANTUM WELL LASERS

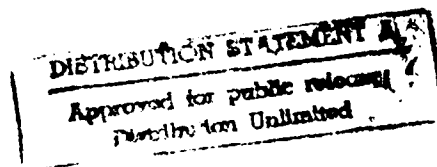
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Submitted under:
Contract #F49620-92-C-0060

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Submitted to:
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
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93-16848
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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 1993		3. REPORT TYPE AND DATES COVERED Final - 15 Aug 1992 - 14 Feb 1993
4. TITLE AND SUBTITLE Ion Doped Quantum Well Lasers			5. FUNDING NUMBERS F49620-92-C-0060	
6. AUTHOR(S) Anton C. Greenwald, Ph.D.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Spire Corporation One Patriots Park Bedford, MA 01730-2396			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Defense Initiative Organization The Pentagon, Washington, DC Air Force Office of Scientific Research, USAF, AFMC Bldg 410, Bolling AFB, DC 20332-6448			10. SPONSORING/MONITORING AGENCY REPORT NUMBER 16C2/C1	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Synthesis of erbium-doped light-emitting structures will make it possible to fabricate electrically excited ionic lasers whose output frequency is independent of temperature. The emission wavelength is determined by the ionic properties of the dopant rather than by the band structure of the semiconductor. Optical pumping efficiency would be high, as would the electrical pumping efficiency of the semiconductor. Spire's approach to fabrication of the required structure is metalorganic chemical vapor deposition (MOCVD). In this research project, Spire synthesized and tested different metalorganic chemical sources for erbium. An amide compound, trimethyl-disilylamino erbium, was found superior to the cyclopentadienyls as it reduced carbon contamination in the final film, without adding nitrogen or silicon contaminants.				
14. SUBJECT TERMS MOCVD, erbium doping, volatile erbium compounds			15. NUMBER OF PAGES 21	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

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SUMMARY

Spire Corporation tested two metalorganic erbium compounds for potential use in metalorganic chemical vapor deposition of doped GaAs and related compounds. One source, previously reported in the literature, was cyclopentadienyl erbium (Cp_3Er). The second source was a new amide compound, $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$, synthesized by the subcontractor, Florida State University.

The Cp compound was purchased from commercial suppliers in very pure form. However, its decomposition path favors residual carbon deposition in the growing film. In all experiments with the erbium Cp source compound diluted in hydrogen, or the same with tetramethyl germane added, the number of carbon atoms in the film always exceeded the number of erbium atoms in the film, sometimes by as much as a factor of ten. Higher deposition temperatures reduced the carbon content but not significantly.

The amide compound, by comparison, left no carbon in the deposited films when oxygen was excluded. Also, there was no trace of nitrogen nor silicon in lower temperature deposition runs. This source material is recommended for doping experiments on GaAs and AlGaAs by MOCVD.

ACKNOWLEDGEMENTS

The synthesis of the new erbium compound described in this work was performed by Professor William S. Rees, Jr, Florida State University, Tallahassee, FL 32306-3006.

This work was sponsored by the Strategic Defense Initiative Organization and monitored by the Air Force Office of Scientific Research under Contract #F49620-92-C-0060.

1 INTRODUCTION

The ability to dope III-V compound semiconductors with rare-earth elements makes it possible to produce ionic luminescence whose wavelength is temperature independent. Diode lasers capable of operating without temperature-stabilizing thermoelectric coolers and feedback control loops are an immediate application of this phenomenon.

Stable erbium-doped GaAs and AlGaAs diode lasers offer particularly great promise because their 1538 nm wavelength matches that needed for efficient pumping of the Er-doped fibers used in optical amplifiers and repeaters.¹ This is not the only advantage Er-doped lasers offer for optical communication systems; because free-carrier lifetime decreases with increasing erbium content, declining to the order of 1 picosecond at 5×10^{19} erbium-ions per cm^3 , very high-speed photonics should be possible with these lasers.^{2,3}

Rare earth doping of III-V semiconductors by melt growth processes has generally led to broad photoluminescence (PL) spectra.^{4,5} Ion implantation doping has produced narrow PL spectra, but results were sensitive to annealing parameters.^{6,7} Because light emitting diodes and lasers are now typically fabricated by metalorganic chemical vapor deposition (MOCVD), and because recent successful results have been reported with rare earth doping of III-V semiconductors by MOCVD,^{8,9,10,11} Spire believes that this is the lowest risk approach to achieving narrow-line, temperature-independent, solid-state light sources.

MOCVD is possible if and only if a volatile erbium source compatible with MOCVD of III-V compounds exists. Finding an improved erbium source was the objective of this research program.

Known volatile sources of erbium include the beta-diketonates, the cyclopentadienyls (Cp), and, developed by this research program, tri-methyl disilyl amides. The structure of beta-diketonates, shown in Figure 1, contains oxygen atoms bonded directly to the metal and could contaminate the semiconductor material. The use of beta-diketones for doping III-V compound semiconductors by MOCVD was reported by Neuhaufen and Wessels without comment on the presence of oxygen.¹¹ The Cp compounds (where $\text{Cp} = \text{C}_5\text{H}_5$), Cp_3Er and $(\text{Me Cp})_3\text{Er}$ used in the reported experiments have low vapor pressures. While successful Er doping of GaAs was reported for low deposition temperatures, yielding narrow peaks in the photoluminescence spectra, higher deposition temperatures are required for optimum growth of AlGaAs for light emitting diodes.

Parameters for known volatile erbium compounds are given in Table I below. Values for the Cp and beta diketonate compounds (first three entries) are taken from the published literature. Sublimation pressures were typically measured when distilling the material under vacuum. Note that all of these source compounds require higher temperatures for sublimation than conventional sources for Al, Ga or As. Also note that all erbium sources will be sublimed from the solid state and are sensitive to atmospheric exposure.

Parameters for $\{\text{N}[\text{Si}(\text{CH}_3)_2]_3\text{Er}$, the new source synthesized for this research, are shown in Table I. This amide compound is more stable and has higher vapor pressure than alternates listed. Use of this material is expected to make fabrication of 1538 nm diode lasers possible.

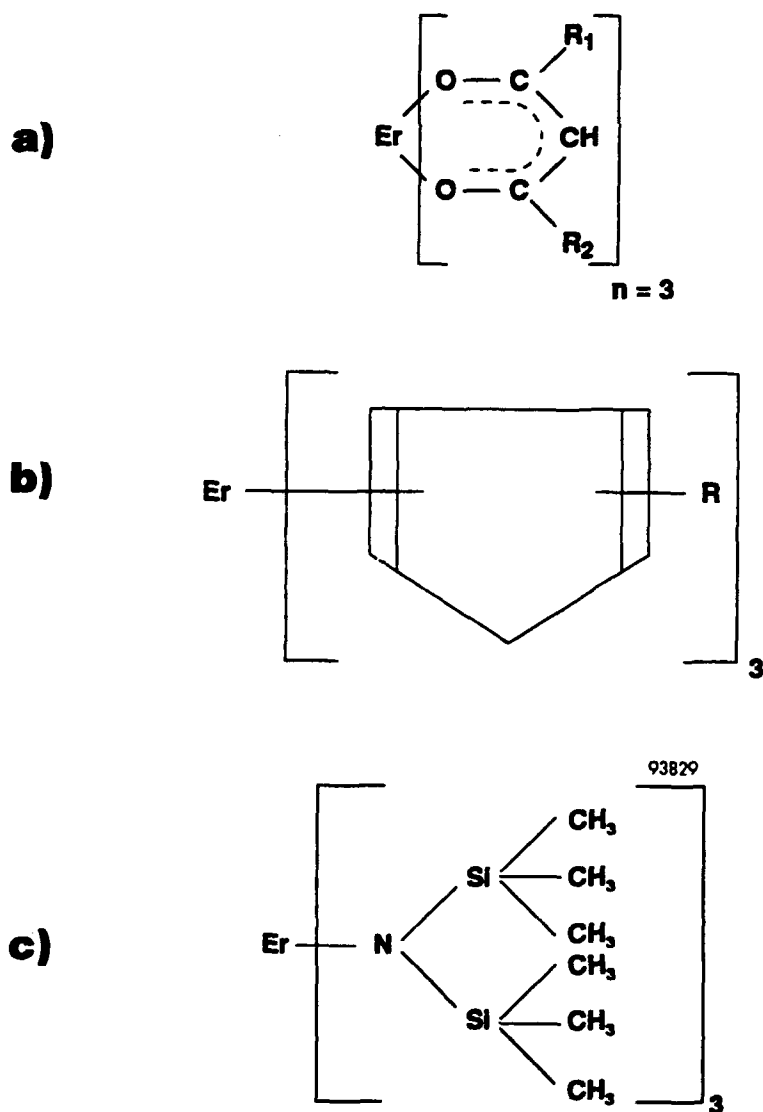


Figure 1 Structure of known volatile metalorganic erbium compounds; a) beta-diketones, (b) cyclopentadienyls, and (c) amides where R_1 , R_2 are organic radical such as H, F, CH_3 , etc.

Table I *Erbium source parameters.*

Source Material	Melt Point °C	Decomposes at (°C)	Vapor Pressure	
			torr	@ °C
$(C_5H_5)_3Er$	285	-	0.01	200
$(CH_3C_3H_5)_3Er$	-	-	0.01	100
$(C_{11}H_{19}O_2)_3Er$	170	290	0.1	160
$\{N[Si(CH_3)_3]_2\}_3Er$	162	300	0.1	120

2 EXPERIMENTAL PROCEDURES

The objective of this research was to identify potential metalorganic source compounds for erbium that do not contain oxygen. This work was very successful in that the amide erbium compound was synthesized for the first time, and proved a potential candidate for MOCVD with reduced carbon contamination. Spire also tested the commercially available compound $(Cp)_3Er$ for comparison and found large carbon contamination, even at elevated temperatures and in a nearly pure hydrogen atmosphere.

The six specific tasks listed in the original proposal were:

- Synthesize ten grams of a volatile Er compound that contains no oxygen; characterize it
- use "standard" MOCVD reactor for decomposition and growth studies
- optimize parameters for reproducible delivery of vapor containing Er to the reactor
- investigate decomposition kinetics as a function of reactor parameters
- characterize erbium films for thickness, composition, and surface morphology
- submit final technical report

All of these six tasks were completed. Spire deposited erbium metal films, and performed erbium test doping of germanium films when possible.

2.1 Chemical Synthesis

The new compound synthesized for this research, whose structure is shown in Figure 1C, was chosen on the basis of previous work with similar materials. The subcontractor reported synthesis of an effective amino zinc compound and its use for CVD.¹² Spire Corporation has tested the equivalent amino lanthanum compound, also synthesized by W.R. Rees, for CVD of lanthanum-nitride.¹³

The starting point for amide synthesis is the compound $\text{LiN}[\text{Si}(\text{CH}_3)_3]_2$ amino-trimethyl lithium. A solution of 20g $\text{HN}[\text{Si}(\text{CH}_3)_3]_2$ (0.124 mole, 26.14 ml) in 300 ml THF is cooled to -78°C using a dry ice and acetone mixture for the bath. At this temperature, 64.6 ml of a $n\text{-BuLi}$ /hexane solution (1.92 mole/liter) is added drop wise. After warming up to room temperature the solution is stirred for two hours and then refluxed for an additional two hours.

This solution is cooled to 0°C and 11.0g of ErCl_3 (40.2 mole) is added in four portions. The ErCl_3 dissolves and the solution now has a pink color. After stirring for 24 hours a white precipitate is formed. All volatiles are removed by sublimation at a pressure of 10^{-2} torr and the residue is extracted with hexanes. The extract is dried by evaporation yielding a pink colored powder.

The key impurity in this pink product is $\text{LiN}[\text{Si}(\text{CH}_3)_3]_2$. The lithium impurity was sublimed to a cold finger at 5×10^{-2} torr and 80°C . The sublimation is repeated several times until no further sublimation is observed. The residue is then sublimed at 10^{-4} torr and 140°C giving a pink amorphous powder.

Results of NMR spectroscopy on this pink product are shown in Figure 2. There is mainly one sharp peak, indicative of a very pure single component material with less than 1 ppm impurity levels. Figure 3 is the thermal gravimetric analysis of the material, showing weight loss as a function of temperature under moderate vacuum (1 torr) conditions. The data indicate that the compound has a high vapor pressure above 175°C , and that there was no residue left to decompose at higher temperatures. A spectroscopic analysis of $\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3\text{Er}$ is shown in Figure 4.

2.2 Sample Preparation

2.2.1 Equipment Description

The MOCVD reactor used for these experiments is shown schematically in Figure 5. the facility was originally used for GaAs/AlGaAs deposition, but has been modified for ceramic use.

Metalorganic sources are stored in bubblers in an evacuated cabinet. The facility has one high temperature bubbler and three low temperature bubblers; the first sits in an oil bath while the last three are kept at constant temperature in water baths. The temperature control for all of these source materials is better than $\pm 0.03^\circ\text{C}$. The reactor also has provision for two carrier gases and one reactive gas. All gas flow rates are measured and controlled by electronic mass flow controllers that are accurate to better than 0.5%. Our implication is that the flow of metallic vapors can be controlled to better than 1% with this system.

The erbium sources were placed one at a time in the high temperature bubbler without separate pressure controls. By maintaining a non-varying flow and non-varying pressure in the exhaust line from this bubbler, the pressure can be steadied for reproducible results, if not accurately measured.

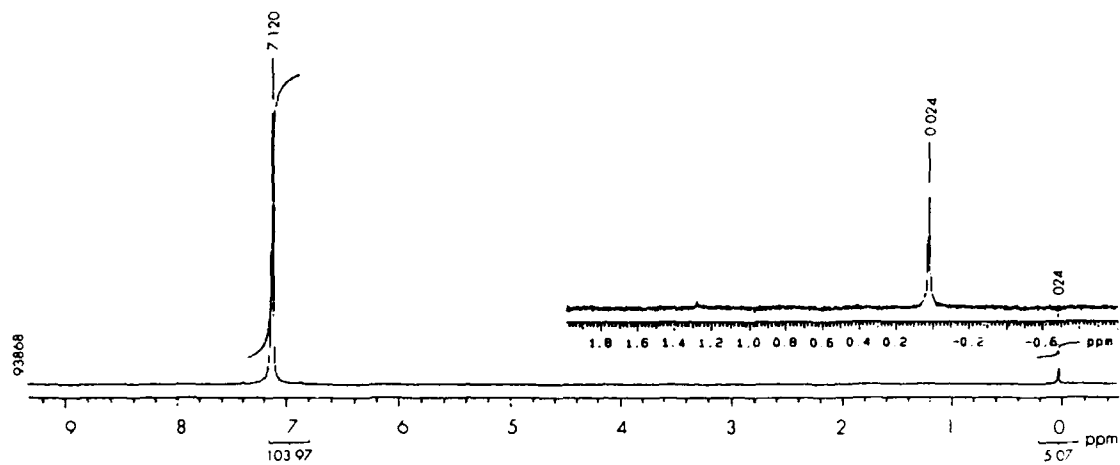


Figure 2 NMR analysis of $\{N[Si(CH_3)_3]_2\}_3Er$ showing very pure, single component material.

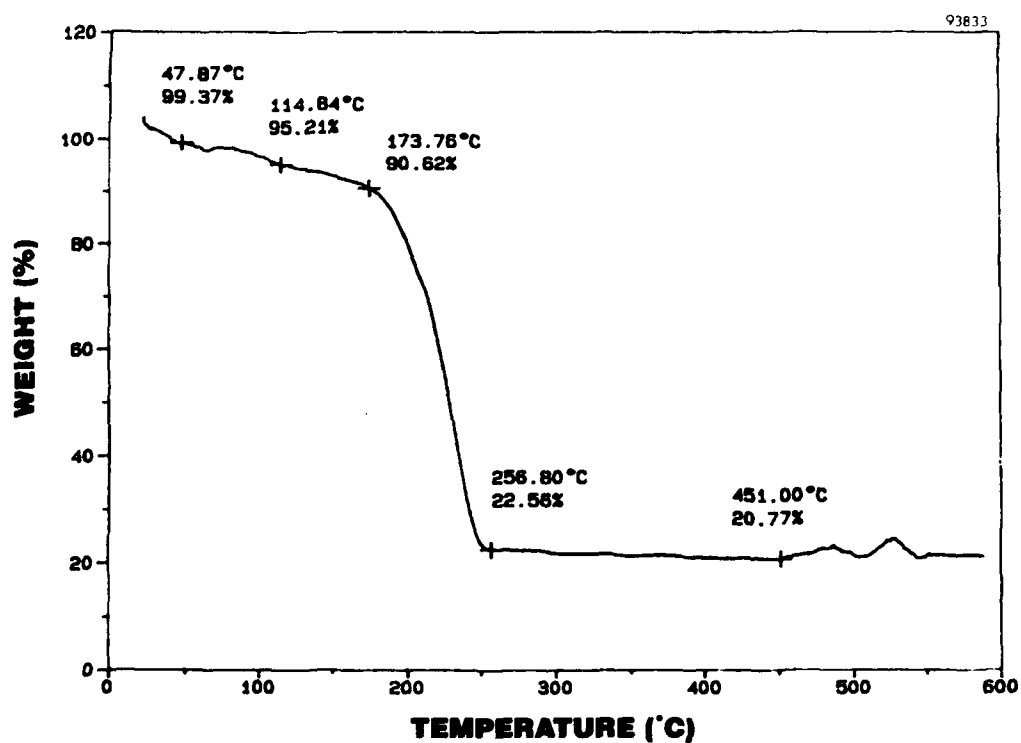


Figure 3 TGA analysis of $\{N[Si(CH_3)_3]_2\}_3Er$.

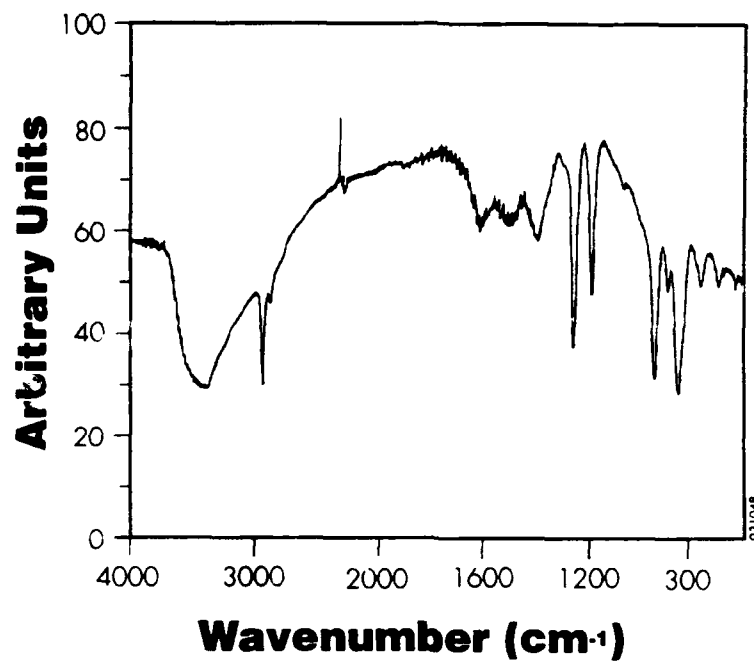


Figure 4 Spectroscopic analysis of $\{N[Si(CH_3)_3]_2\}_3Er$.

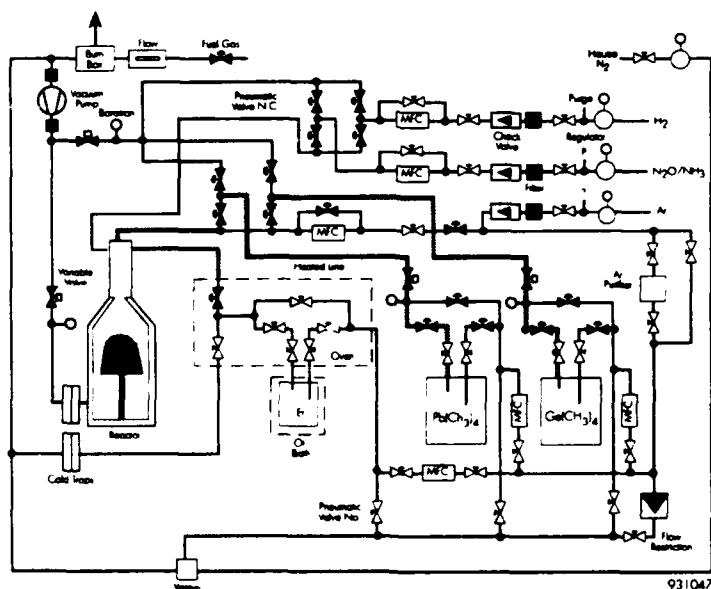


Figure 5 Schematic diagram of MOCVD reactor.

The pressure in the reactor and vent lines was controlled by separately monitors and adjustable valves. The temperature in the reactor was controlled to within 1°C. The sample was heated by resistance heaters at low pressure. Induction heating is available and used for GaAs deposition, but cannot be used below 50 torr in this geometry.

2.2.2 Tris-cyclopentadienyl erbium

The first source tested was Cp_3Er , purchased directly from a commercial supplier. The source bubbler was maintained at 200°C. All gas lines from that point to the reactor were heated to 210°C to prevent condensation in the lines. Depositions were carried out at either 10 or 75 torr, and at substrate temperatures from 650 to 825°C to simulate the range of parameters used for AlGaAs deposition.

Spire could not add arsine in this reactor. To show semiconductor doping effects with similar compounds, we added erbium to tetramethyl germane. The compound has a similar structure to trimethyl gallium or trimethyl aluminum used for standard CVD growth of AlGaAs films.

Carbon contamination is very evident in Figures 6, 7 and 8 showing results of films deposited with $(\text{Cp})_3\text{Er}$. Figure 6 is the raw spectral output of Rutherford Backscattering Spectroscopy (RBS) analysis. The points are measured data while the curve is a fit to this data for composition as a function of depth. The top layer contains more than ten times as many carbon atoms as erbium atoms. There is little oxygen or nitrogen, and hydrogen is not detected by this technique.

Auger spectroscopy of the identical film is shown in Figure 7. The relative abundance of elements in Auger data are not calibrated and the RBS data is more accurate. The film is very thin, under 50 nm, and has exhibited island growth with less than 100% substrate coverage at this point. Thus SiO_2 from the substrate surface is detected. In Figure 8 the same data is presented for $(\text{Cp})_3\text{Er}$ doping of a germanium film grown from $[\text{CH}_3]_4\text{Ge}$ at 825 °C. Again note the large carbon contamination showing effective deposition of germanium-carbide, doped with erbium. As a positive note, we achieved erbium concentrations of nearly 5% (uncalibrated) in the semiconductor material.

2.2.3 Tris-amido-disilyltrimethyl Erbium

The amido-erbium source was delivered to Spire before accurate measurements of the parameters given in Table I were available, and before good TGA data, Figure 7, was confirmed. Our initial guess for source parameters was a temperature of 150°C. At this source temperature the vapor pressure was too low to observe any film deposition. The temperature was raised to 175°C, just below the point where one expects significant decomposition, but attains the maximum vapor pressure.

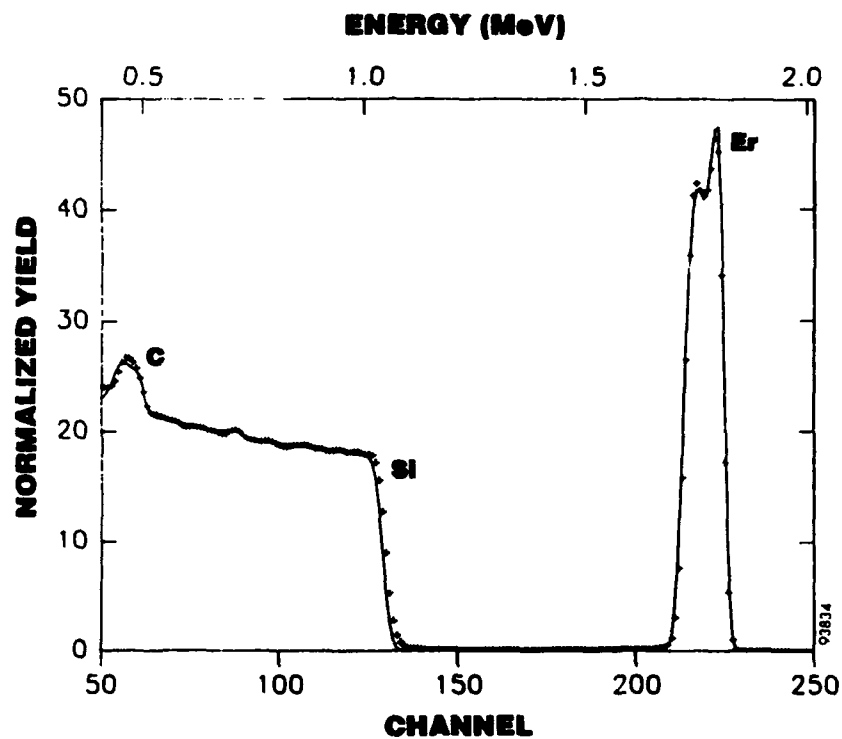


Figure 6 RBS analysis of erbium metal film at 600°C from $(Cp)_3Er$ in hydrogen onto silicon substrate showing preponderance of carbon contamination.

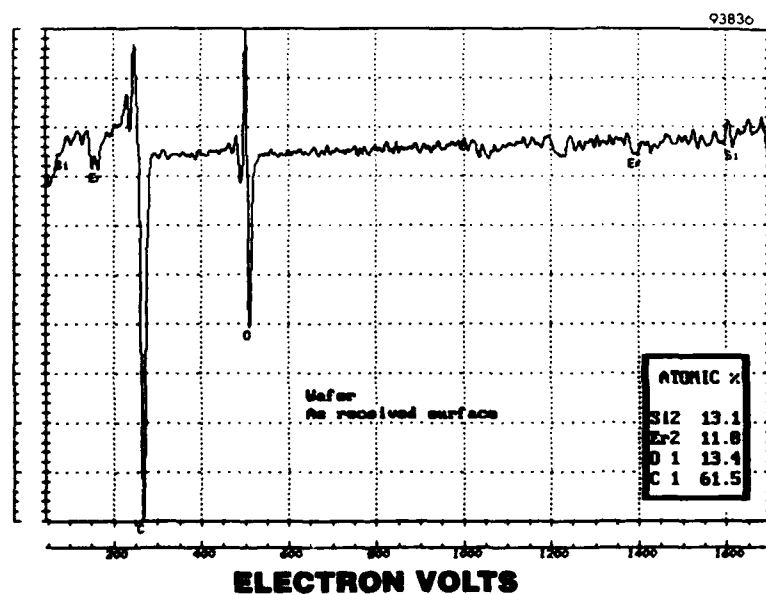


Figure 7 Auger analysis of the sample in Figure 9 showing excessive carbon contamination in an erbium film deposited from the Cp source.

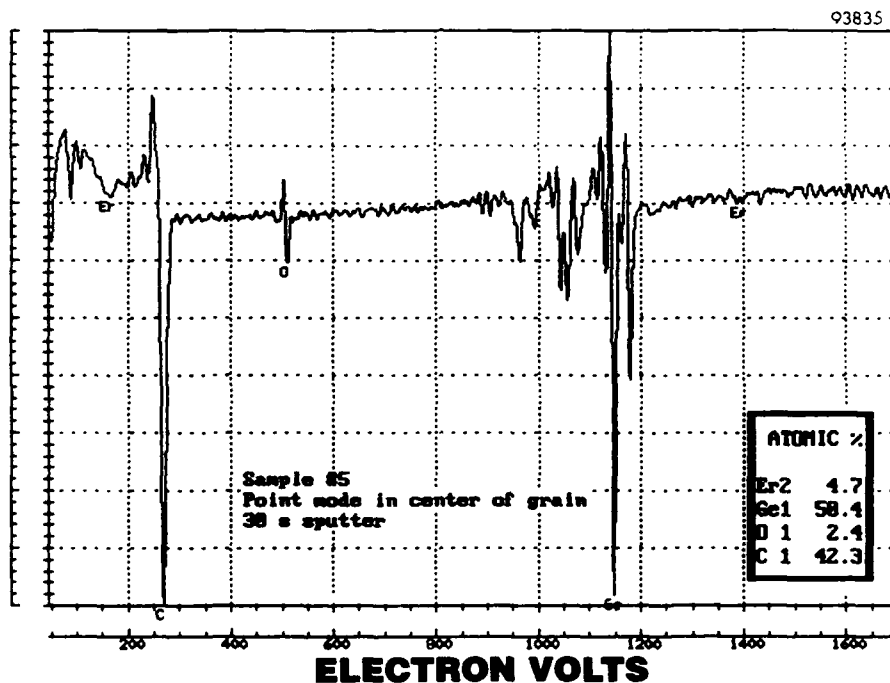


Figure 8 Auger spectroscopy analysis of an erbium doped germanium film showing excessive carbon contamination from $(Cp)_3Er$.

The change with the amide source is shown in Figure 9. This is an Auger spectroscopy analysis of the as received surface of a very thin (4 nm) erbium film deposited at 600°C from $\{N[Si(CH_3)_2]_2\}_3Er$. The film does not fully cover the silicon substrate giving a large SiO_2 signal. Also, the surface was not cleaned of carbon contamination normally present whenever a sample is transported from one site to another in air, because this would have removed the very thin erbium film. The amount of carbon present can be wholly attributed to this carbon contamination from the atmosphere. In any case, the carbon content of the film in Figure 9 is very much less than the carbon content of the film in Figure 7. Use of an amide compound has significantly reduced carbon contamination. Technical difficulties prevented completion of germanium doping experiments.

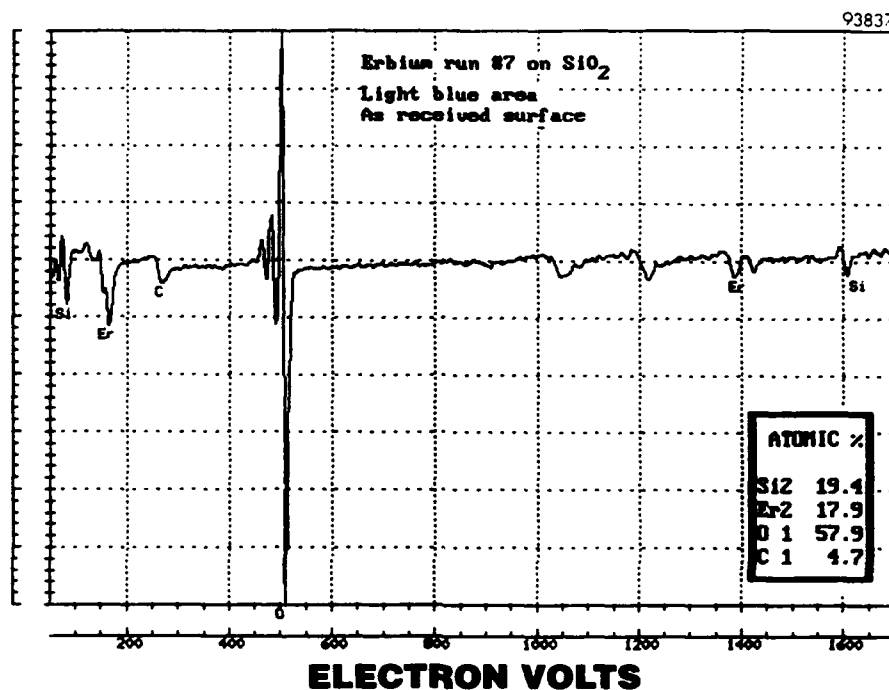


Figure 9 *Auger spectroscopy analysis of incomplete 4 nm erbium film on silicon dioxide deposited with erbium amide source showing significant reduction of carbon content.*

3 CONCLUSIONS

The new source material, $\{N[Si(CH_3)_3]_2\}_3Er$, tested for use with MOCVD of III-V compounds is advantageous compared to existing commercially available reagents as we expect much less carbon contamination in the final semiconductor film. This compound is recommended for use in the next phase of the research: fabrication of Er doped diode lasers emitting at 1538 nm.

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13. Contract DNA001-91-C-0089 with the Defense Nuclear Agency.

APPENDIX A

Pre-print of paper submitted for publication in "Rare Earth Doped Semiconductors," ed. G.S. Pomrenke, P.B. Klein and D.W. Langer (Material Research Society Symposium Proceedings, 301, 1993). Paper E1.3 to be presented in San Francisco Meeting April 1993.

MOCVD ERBIUM SOURCES

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ABSTRACT

The overall objective of this research is to develop source materials for doping AlGaAs. We compared $\text{Er}(\text{C}_5\text{H}_5)_3$ to $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_2]_2\}_3$ for purity, decomposition kinetics and doping of germanium films deposited from $\text{Ge}(\text{CH}_3)_4$ in a hydrogen atmosphere. Cyclopentadienyl erbium left large amounts of carbon in pure metal films, and in the germanium film, at low pressure and temperatures to 850°C. The amide compound decomposed cleanly without carbon, nitrogen or silicon in the deposited film.

INTRODUCTION

The ability to dope III-V compound semiconductors with rare-earth elements could make it possible to produce ionic luminescence whose wavelength is temperature independent. Stable erbium-doped GaAs and AlGaAs diode lasers offer particularly great promise because their 1538 nm wavelength matches that needed for efficient pumping of the Er-doped fibers used in optical amplifiers.¹

Rare earth doping of III-V semiconductors by melt growth processes has generally led to broad photoluminescence (PL) spectra.^{2,3} Ion implantation doping has produced narrow PL spectra, but results were sensitive to annealing parameters.⁴ Because light emitting diodes and lasers are now typically fabricated by metalorganic chemical vapor deposition (MOCVD), and because recent successful results have been reported with rare earth doping of III-V semiconductors by MOCVD,⁵⁻⁸ this approach to achieving narrow-line, temperature-independent, solid-state light sources has reduced risk.

MOCVD is possible if and only if a volatile erbium source compatible with MOCVD of III-V compounds exists. Finding an improved erbium source that contained no oxygen was the objective of this research program. Possible volatile erbium compound structures are shown in Figure 1. The betadiketonates (Figure 1a) contain oxygen and were not considered. $\text{Er}(\text{C}_5\text{H}_5)_3$ and $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_2]_2\}_3$ (Figures 1b and 1c) were tested.

SYNTHESIS

The cyclopentadienyl erbium material was purchased from a commercial vendor, tested impurity levels were below 1 ppm. The amide was investigated after good results were reported for MOCVD of ZnSe using similar precursors.⁹ $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_2]_2\}_3$ was synthesized from $\text{LiN}[\text{Si}(\text{CH}_3)_2]_2$ and ErCl_3 , forming lithium chloride and the erbium-amide.¹⁰ The principal impurity in the resulting product is $\text{LiN}[\text{Si}(\text{CH}_3)_2]_2$, which was separated out by successive sublimations at 5×10^{-2} torr and 80°C. The final residue was sublimed at 140°C, giving a pink powder. The purity of this product is shown in Figure 2, NMR analysis. The single very sharp peak implies a total contaminant concentration less than 0.1 ppm.

Decomposition kinetics of $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_2]_2\}_3$ are shown in the thermal gravimetric analysis (TGA) in Figure 3. The decomposition point of this material is at 257°C. It sublimed rapidly at 175°C. Measured melt point was 162°C, and the vapor pressure measured at 120°C was 0.1 torr. For comparison, the published vapor pressure of $\text{Er}(\text{Cp})_3$ is 0.01 torr at 200°C, and the melt point is 285°C.

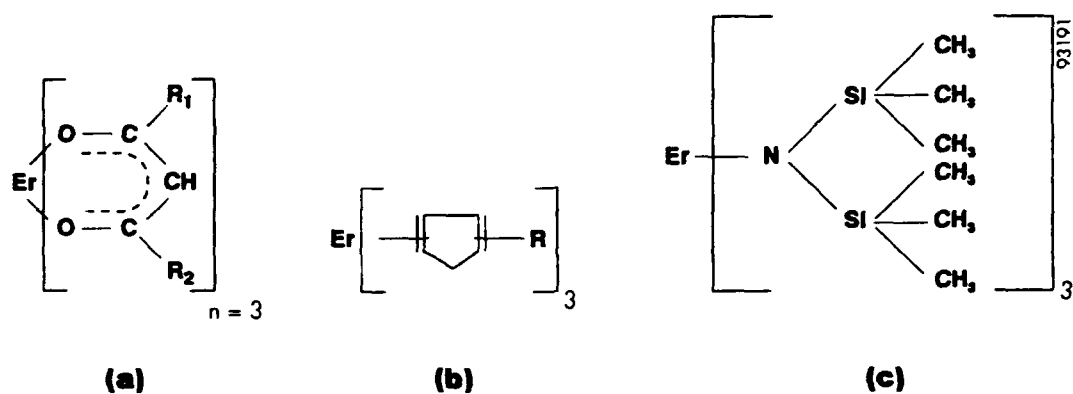


Figure 1 Structure of metalorganic erbium source chemicals, a) beta-diketonates, b) cyclopentadienyls, and c) amino-silyls.

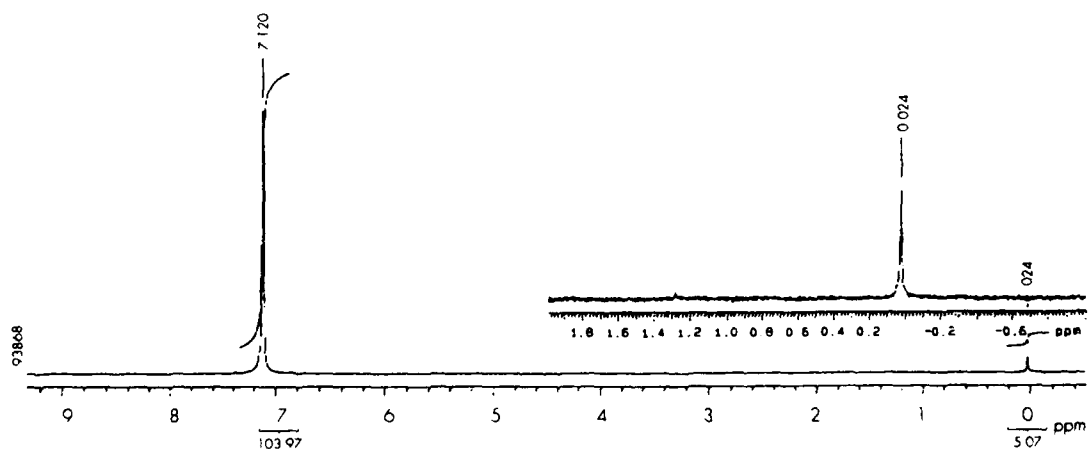


Figure 2 NMR analysis of $Er\{N[Si(CH_3)_3]_2\}_3$ showing very pure material.

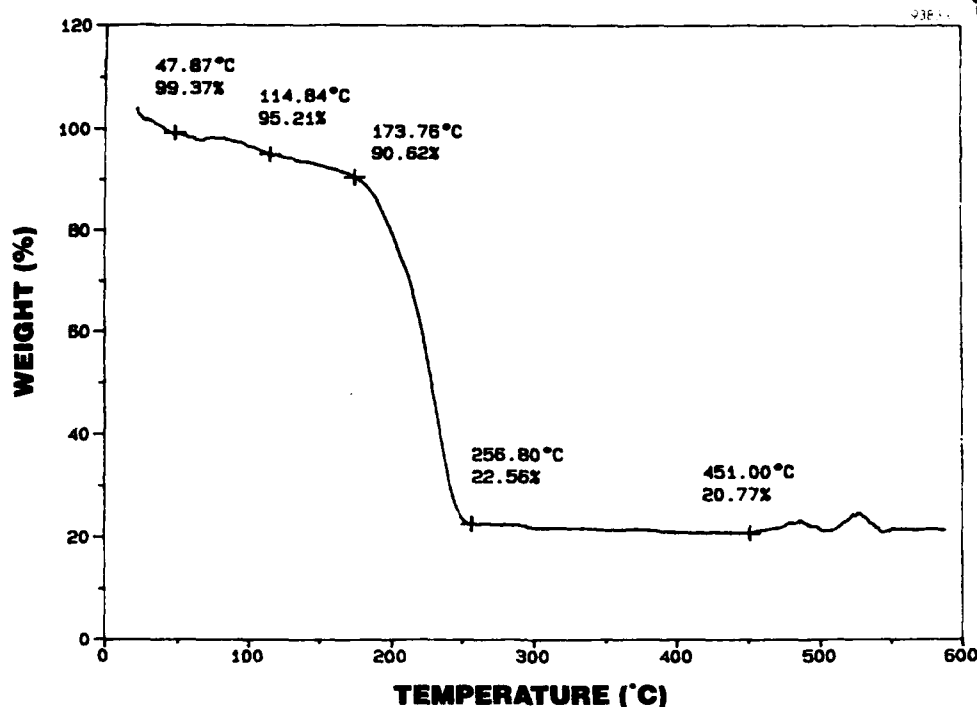


Figure 3 TGA analysis of $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$.

CHEMICAL VAPOR DEPOSITION

As the objective of this work is to dope AlGaAs compounds with erbium, the sources were tested at parameters appropriate for epitaxial growth of these III-V compounds. All CVD tests were performed in a hydrogen atmosphere using argon as the carrier gas. The reactor pressure was maintained at either 10 or 75 torr with induction heating of the susceptor to temperatures between 650 and 850°C.

The erbium sources were stored in a stainless steel bubbler without teflon liner present in some designs. The bubbler was fitted with high temperature valves as were all valves used downstream from these erbium sources. The manifold carrying the erbium vapor was heated in an oven typically 10°C above the temperature of the source to prevent condensation in the lines. The oven assured more uniform temperatures for the valves than the use of heating tape. The gas line from the manifold to the reactor, which contained no valves, was heated by resistance tape to the same temperature as the manifold. There were no deposits in any of the valves or lines except right at the exit slit to the reactor, which could not be directly heated.

Two experiments were performed with each erbium source, deposition of erbium metal alone, and doping a germanium film deposited from $\text{Ge}(\text{CH}_3)_4$. The liquid germanium source had a very high vapor pressure and the pressure of the bubbler holding this compound was separately monitored.

CVD results for the $(\text{Cp})_3\text{Er}$ compound are shown in Figures 4 and 5. The erbium source was maintained at a temperature of 200°C. With a carrier flow of 200 sccm diluted by 4.8 slpm of hydrogen, a metal film 400 nm thick was deposited in two hours at 600°C. The film composition was measured by Rutherford Backscattering Spectroscopy (RBS). Dots in Figure 4 are measured data points while the line is fit using a multilayered model. Carbon content of this film exceeded 90% by atomic ratio.

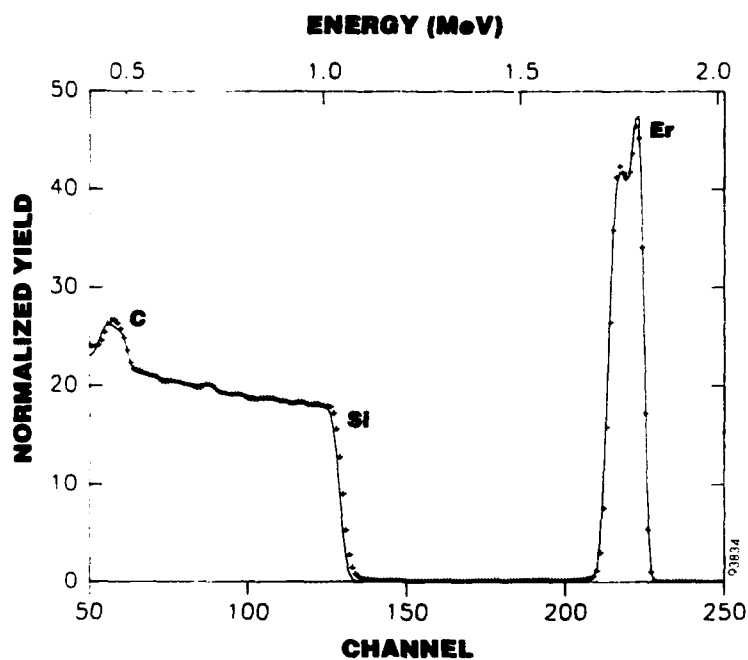


Figure 4 RBS analysis of carbon contaminated erbium film deposited at 600°C from $\text{Er}(\text{Cp})_3$ onto a silicon wafer.

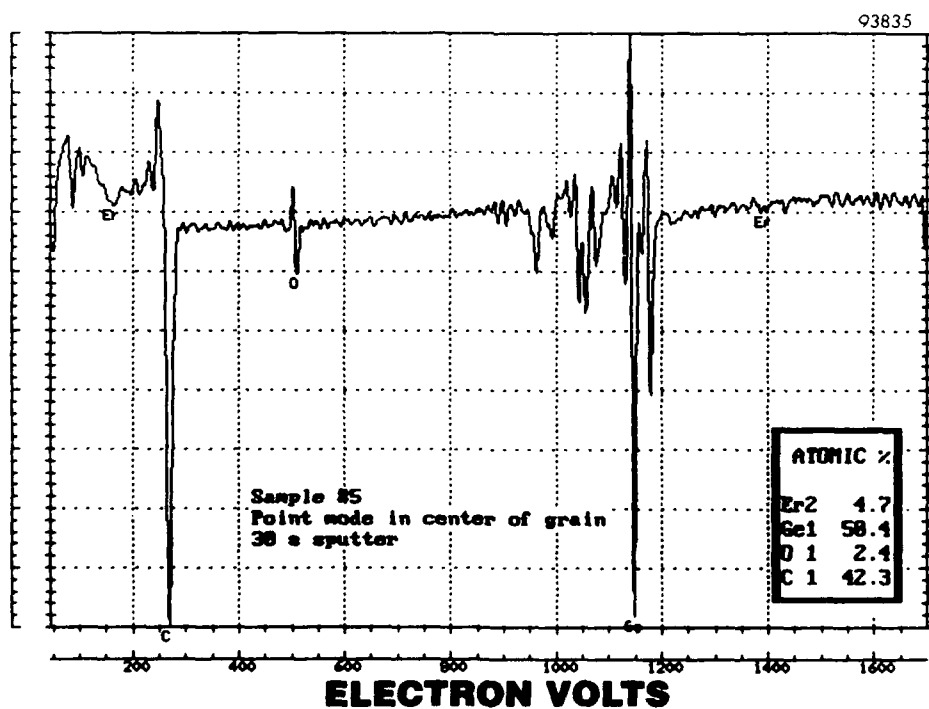


Figure 5 Auger spectroscopy of erbium doped germanium film deposited from $\text{Er}(\text{Cp})_3$, showing excess carbon contamination.

The Auger Spectroscopy data in Figure 5 was a doped germanium film. Deposition parameters were 825°C at a carrier flow rate of 100 sccm for the erbium source, 20 sccm for the germanium source kept at -5°C, at a pressure of 75 torr and total flow (balance hydrogen) of 5 slpm. It was believed that higher temperatures would reduce the carbon in the film. As shown in Figure 5, however, nearly stoichiometric germanium-carbide was deposited with a few percent erbium doping. Although the composition of the Auger data was not calibrated, it does not change our conclusion, this is a poor source to use for MOCVD.

The difference with the erbium amide compound is shown by the Auger spectroscopy data in Figure 6. Initial tests with the amide at 150°C source temperature produced no visible deposits at substrate temperatures of 400 and 600°C. The source temperature was raised to 175°C (see Figure 3) and a thin (4 nm) film was formed on a silica coated wafer. The as-received surface is shown in Figure 6, sputtering removed the film. The carbon content is typical of atmospheric contamination of any sample not cleaned by sputtering. The silica on the surface indicates that the deposition is of an island growth nature, and complete coverage has not been reached yet. These erbium compounds react with oxygen at low temperatures, and accidental exposure contaminated the amide source and prevented further work.

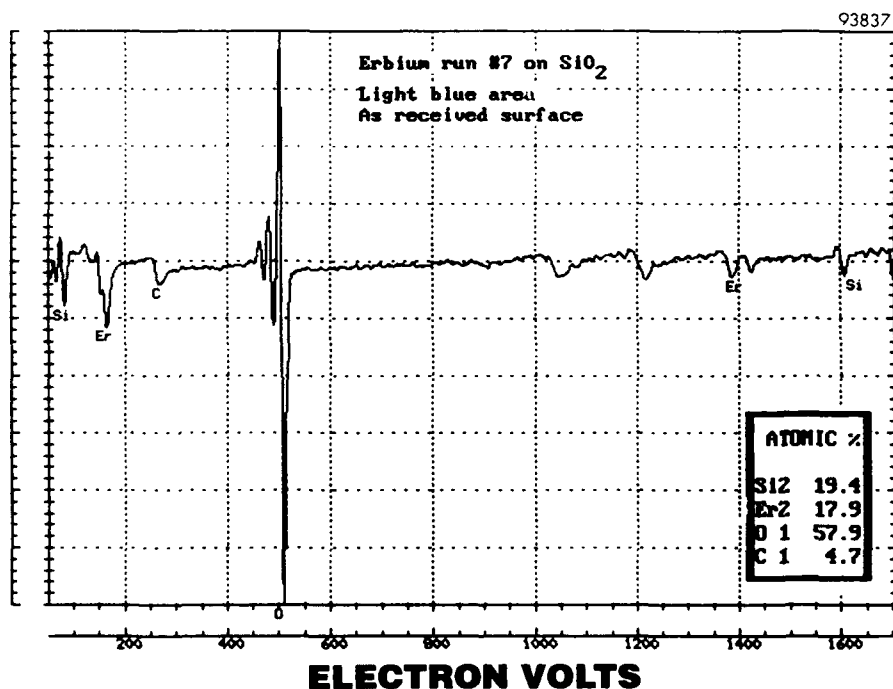


Figure 6 Auger spectroscopy of erbium film deposited from the amide compound showing significant decrease (possible zero without atmospheric contamination) in carbon content.

CONCLUSIONS

The amide compound decomposed with little trace of silicon, nitrogen, or carbon contamination. It is preferred as a source for MOCVD of GaAs compared to the cyclopentadienyl compound, which left large amounts of carbon in the film with or without semiconducting metalorganics present.

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